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ORIGINAL

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Patents Act 1990

PROVISIONAL SPECIFICATION

Invention Title: "Hydrometallurgical Processing of Manganese Containing Materials"

The invention is described in the following statement:

"Hydrometallurgical Processing of Manganese Containing Materials"

Field of the Invention

The present invention relates to the hydrometallurgical processing of manganese containing materials. More particularly, the process of the present invention is intended to allow efficient hydrometallurgical processing of low-grade manganese dioxide feedstock to produce manganese chemicals, including electrolytic manganese dioxide.

Background Art

It is generally known that manganese may be leached from manganese dioxide containing ores using sulphur dioxide. However, the sulphur dioxide leaching of manganese dioxide containing materials is also known to produce by-product dithionate ion levels of >5g/l. These levels may be far higher depending upon the amount of manganese being leached. For example, levels of about 20g/l are not uncommon. Interestingly, it is reported in Cotton and Wilkinson, Advanced Inorganic Chemistry, 3rd Edition at page 452, that "the method for production of dithionate or dithionic acid is the reaction between sulphur dioxide or sulphite with manganese dioxide in the presence of acid".

Low grade manganese dioxide feedstock (<40% Mn) are presently uneconomic to process using conventional roast-reduction and sulphuric acid leaching to produce manganese sulphate. High grade ores (>40% Mn) are needed to justify the economics of the roast reduction process. Presently, all leaching of manganese dioxide containing materials using sulphur dioxide leads to the formation of >5g/l levels of dithionate ions in solution. With dithionate ion levels of this magnitude it is generally necessary to incorporate into any flow sheet a high capital cost stage, being "oxidation" or "aging". The long residence times required to "oxidise" the dithionate ion from the >5g/l levels down to lower than 1g/l are highly capital intensive.

Failure to control dithionate levels in the production of a manganese sulphate crystal product has previously led to the manganese dithionate contaminant in that product slowly reacting to release sulphur dioxide gas.

It would prove advantageous to provide a process whereby low-grade manganese dioxide containing materials or feedstock could provide manganese sulphate leach solutions with a level of dithionate ion less than about 5g/l, and preferably less than 1g/l.

The ability to recover manganese dioxide from low-grade feedstocks will avoid or at least reduce the need for further manganese ore mining and land disturbance, bringing various environmental benefits. For example, the utilisation of manganese tailings allows for conservation of existing resources.

Further, the use of a hydrometallurgical route for the reduction of Mn(IV) negates the need for the use of gas fired kilns or fluid bed reactors, feed stocks no longer need to be heated to about 1000°C and then cooled prior to leaching, and there is lesser need for carbon input, which in turn results in lower greenhouse gas emissions.

Still further, the use of the relatively easily controlled hydrometallurgical route allows monitoring of the solution potential of the leach solution or slurry thereby indicating complete dissolution of Mn(IV). The use of the sulphur dioxide leach provides complete conversion of Mn(IV) to Mn(II), thereby avoiding the production of leachable manganese species in solid residues.

In particular, if it is desired to produce electrolytic manganese dioxide ("EMD"), solutions containing elevated dithionate ion levels result in chemical reactions occurring that effect the quality and purity of the EMD produced in the electrowinning cells. Also, hydrogen sulphide is evolved, bringing with it certain occupational health and environmental issues.

The preceding discussion of the background art is intended to facilitate an understanding of the present invention only. It should be appreciated that the

discussion is not an acknowledgement or admission that any of the material referred to was part of the common general knowledge in Australia as at the priority date of the application.

Throughout the specification, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Disclosure of the Invention

In accordance with the present invention there is provided a process for the hydrometallurgical processing of manganese containing materials, the process comprising the formation of a slurry of manganese dioxide containing feedstock and acidic solution, passing a volume of sulphur dioxide gas through the leach solution whereby the levels of dithionate ion generated in the leach are less than about 5g/l.

Preferably, the levels of dithionate ion generated in the leach solution are less than about 1g/l.

Still preferably, the pH of the leach solution is maintained at less than about 1.5.

In one form of the invention the leach solution comprises a slurry of manganese dioxide containing material at a slurry density of less than about 10%w/v, less than about 120g/l manganese sulphide, a temperature of greater than about 95°C, and at a pH of less than about 1.5.

In another form of the invention the manganese dioxide containing feedstock contains less than 40% manganese.

Preferably, the leach solution has an initial soluble iron concentration of greater than 4g/l. The iron is preferably in the form of ferric sulphate ($Fe_2(SO_4)_3$). The

ferrous concentration is preferably maintained at a level below about 0.5g/l by providing an excess or residual amount of manganese dioxide in the slurry.

The ratio of ferric to ferrous may be monitored throughout the leach to ensure an oxidation reduction potential (ORP) of 550mV, or above (vs Ag/AgCl reference electrode).

The sulphur dioxide gas is preferably passed through the leach solution over a period of at least 10 hours whereby up to about 95% of manganese dioxide is dissolved. Preferably, the leach is conducted over a period of between about 10 to 15 hours.

Preferably, once a stoichiometric amount of sulphur dioxide has been added to the leach solution to achieve a 95% dissolution of the manganese dioxide present, the reaction is halted.

In accordance with present invention there is further provided a process for the production of electrolytic manganese dioxide, the process comprising a leach of a manganese dioxide containing feedstock in acidic solution, through which a volume of sulphur dioxide gas is passed, and in which dithionate ion levels are maintained at less than about 5g/l, the resulting leach solution being processed to provide an appropriate electrolyte that is passed to an electrowinning stage during which electrolytic manganese dioxide is deposited.

Preferably, the levels of dithionate ion generated in the leach solution are less than about 1g/l.

Still preferably, the pH of the leach solution is maintained at less than about 1.5.

In one form of the invention the leach solution comprises a slurry of manganese dioxide containing material at a slurry density of less than about 10%w/v, less than about 120g/l manganese sulphate, a temperature of greater than about 95°C, and at a pH of less than about 1.5.

In another form of the invention the manganese dioxide containing feedstock contains less than 40% manganese.

Preferably, the leach solution has an initial soluble iron concentration of greater than 4g/l. The iron is preferably in the form of ferric sulphate ($Fe_2(SO_4)_3$). The ferrous concentration is preferably maintained at a level below about 0.5g/l by providing an excess or residual amount of manganese dioxide in the slurry.

The ratio of ferric to ferrous may be monitored throughout the leach to ensure an oxidation reduction potential (ORP) of 550mV, or above (vs Ag/AgCl reference electrode).

The sulphur dioxide gas is preferably passed through the leach solution over a period of at least 10 hours whereby up to about 95% of manganese dioxide is dissolved. Preferably, the leach is conducted over a period of between about 10 to 15 hours.

Preferably, once a stoichiometric amount of sulphur dioxide has been added to the leach solution to achieve a 95% dissolution of the manganese dioxide present, the reaction is halted.

Preferably, the acidic solution used in the leach is at least in part comprised of return or spent sulphuric acid solution from the electrowinning stage. It may be necessary to add additional acid to the leach to ensure the pH remains less than about 1.5.

Brief Description of the Drawings

The present invention will now be described, by way of example only, with reference to one embodiment thereof and the accompanying drawings, in which:-

Figure 1 is a schematic flow chart of a process for the production of an electrolytic manganese dioxide product from a low grade manganese feedstock in accordance with the present invention;

Figure 2 is a graphical representation of the percentage manganese "leached" relative to SO_2 addition and Eh during the leach conducted within the process of Figure 1; and

Figure 3 is a graphical representation of the percentage manganese "leached" over time and relative to SO_2 additional during the leach of Figure 2.

Best Mode(s) for Carrying Out the Invention

In Figure 1 there is shown a process 10 for the production of electrolytic manganese dioxide product in accordance with the present invention. A manganese dioxide ore feedstock 12, containing about 34% manganese, is initially milled in a wet ball mill 14 prior to the generated slurry being passed to a leach 16 conducted in at least one agitated reactor.

In addition to the milled feedstock slurry the leach 16 is fed with return sulphuric acid electrolyte 17 from an electrowinning stage 18 to form a leach solution. The leach solution has a volume of sulphur dioxide gas 20 passed therethrough, the sulphur dioxide gas 20 being formed through a sulphur burning step 22, in which sulphur is burnt in oxygen to generate sulphur dioxide.

The slurry density of the feedstock fed from the mill 14 is less than 10% w/v. The slurry is both heated and agitated, as the leach solution, once within the or each reactor 16. The concentration of manganese sulphate ($MnSO_4$) in the leach solution is <120g/l whilst the temperature of the leach solution is >95°C. The leach solution is maintained at a pH of less than about 1.5.

The leach solution within the leach 16 has an initial soluble iron concentration of >4g/l. The iron is in the form of ferric sulphate ($Fe_2(SO_4)_3$). The ferrous concentration is maintained at less than 0.5g/l by ensuring there is always an excess or residual amount of manganese dioxide in the leach.

The leach is conducted over a period of 10 to 15 hours by passing a volume of sulphur dioxide gas through the leach solution. The rate at which the sulphur dioxide is passed through the leach solution is governed by the requirement that up to 95% of the manganese dioxide in the slurry fed to the leach 16 is dissolved/solubilized over the period of 10 to 15 hours. It is envisaged that longer time periods may be utilised.

The ratio of ferric to ferrous in the leach 16 is monitored by an ORP probe. A minimum value of 550mV is required (vs Ag/AgCl reference electrode). If the ORP value falls below 550mV more feedstock slurry is added to the leach 16.

It is believed that the predominant leaching reaction proceeds as follows:

$$MnO_2 + SO_2 = MnSO_4$$

However, it is understood that whilst the process of the present invention ensures that the production of manganese sulphate is the predominant reaction, a trace of dithionate is still generated. The production of dithionate is believed to proceed as a free radical combination reaction as follows:

$$SO_3^{\cdot -} + SO_3^{\cdot -} = S_2O_6^{2-}$$

High pH values favour the production of dithionate. As such, the pH of the leach 16 is maintained at less than about 1.5, as noted hereinabove.

Once a stoichiometric quantity of sulphur dioxide 20 has been fed through the leach solution, whereby a maximum of 95% of the manganese dioxide present is dissolved/solubilized, the reaction is halted by withdrawing the sulphur dioxide 20 feed to the leach 16. The stoichiometric addition of SO_2 is represented graphically in Figure 2 relative to the % manganese leached and the Eh, showing that the Eh or solution potential provides an accurate indication of completion of the manganese (IV) dissolution reaction, whilst Figure 3 demonstrates the effect of sulphur dioxide addition on the % manganese leached over time.

It is envisaged that the sulphur dioxide 20 might also be provided as a waste gas from a smelting or an industrial process. Further, the sulphur dioxide might be added to the leach solution as a sulphite solution (SO_3^{2-}).

The remainder of the process 10 for the production of EMD involves the passing of pregnant leach solution to a jarositing step 22 to reduce potassium and sodium levels as desired. A goethiting step 24 is then used to reduce iron levels to sub-ppm levels through the addition of ground limestone. A solid/liquid separation step is then used, involving both thickening 26 and filtration 28.

Solids from the filtration 28 are washed to reclaim any residual manganese sulphate solution, this being fed back to the leach 16 to make up any volume lost from the return electrolyte 17 to a manganese sulphate bleed stream 30. This bleed stream 30 allows manganese sulphate to be concurrently produced for use in fertilisers, for example.

Overflow from the thickening 26 is passed to a sulphiding step 32 for the removal of heavy metals, including nickel, cobalt and molybdenum. Following the sulphiding step 32 the heavy metal sulphides are removed by pressure filtration 34 and the electrolyte from the electrowinning step 18 held in storage tanks 36.

The electrowinning step 18 then proceeds utilising submerged titanium anodes, tubular copper cathodes and a totally wax free environment. Fully laden anodes are harvested on a two-weekly cycle with resulting EMD chip being passed to produce processing and packaging operations.

It is envisaged that the process of the present invention, specifically as it resides in the leaching of manganese containing feedstocks to produce leach solutions with dithionate ion levels of less than 5g/l, and preferably less than 1g/l, may by applied to the processing of all types of manganese dioxide containing ores (including both high and low grade), mine tailings, fines, fumes and tailings of manganese ferro-alloy production facilities, ocean floor manganese nodules, ferromanganese nodules, wastes from zinc refinery cells and manganese dioxide contained in used or partially used alkaline or carbon zinc batteries. The leach

solutions generated by reprocessing such materials in accordance with the present invention can then be purified and used in the production of EMD, EMM and other manganese chemical products.

Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of the present invention.

Dated this Tenth day of October 2002.

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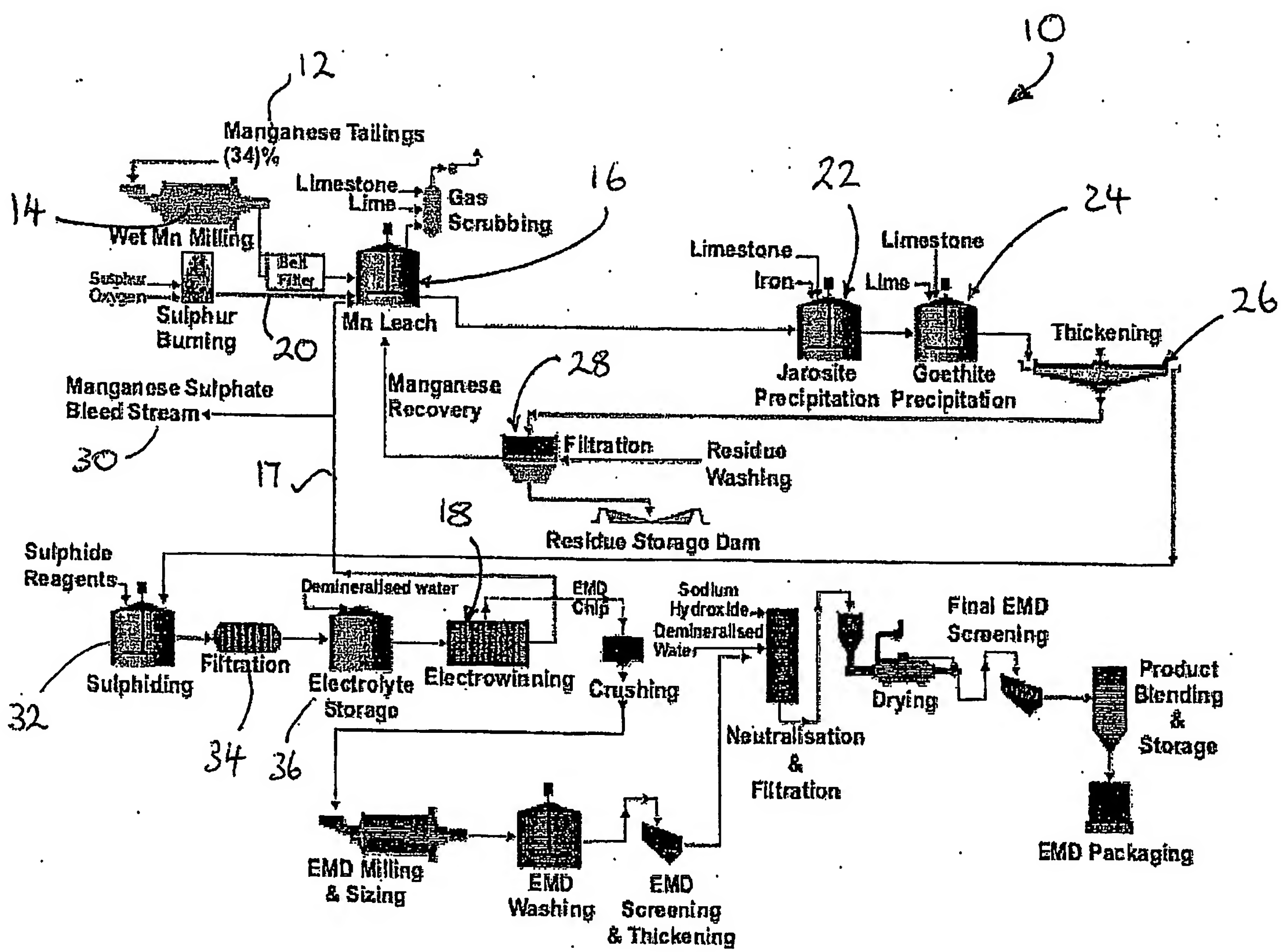

10
12
Manganese Tailings (34)%
14
Wet Mn Milling
Sulphur
Oxygen
Sulphur Burning
Belt Filter
20
Limestone
Lime
Gas Scrubbing
16
Mn Leach
22
Limestone
Iron
Jarosite Precipitation
24
Limestone
Lime
Goethite Precipitation
26
Thickening
Manganese Sulphate Bleed Stream
30
Manganese Recovery
28
Filtration
Residue Washing
Residue Storage Dam
17
18
Sulphide Reagents
Sulphiding
32
Filtration
34
Electrolyte Storage
36
Demineralised water
Electrowinning
EMD Chip
Crushing
Sodium Hydroxide
Demineralised Water
Neutralisation & Filtration
Drying
Final EMD Screening
Product Blending & Storage
EMD Packaging
EMD Milling & Sizing
EMD Washing
EMD Screening & Thickening

Figure 1

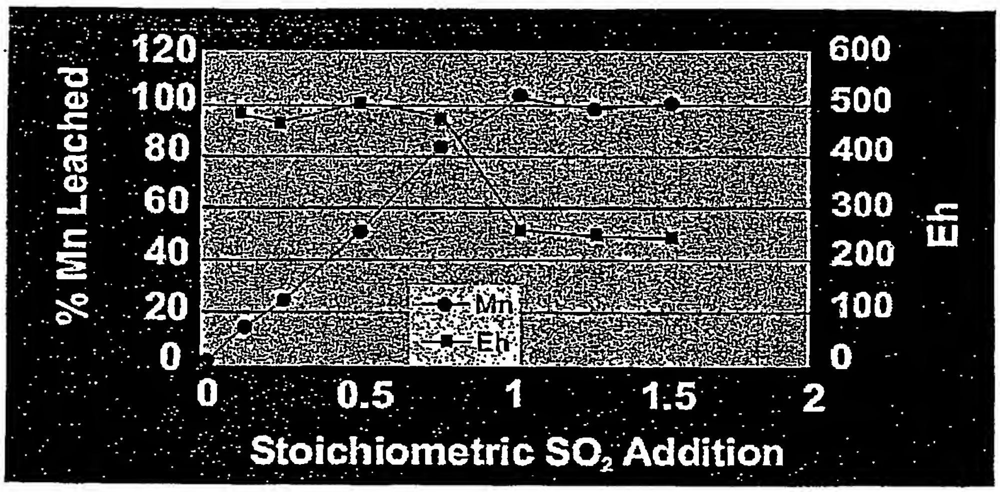

Figure 2

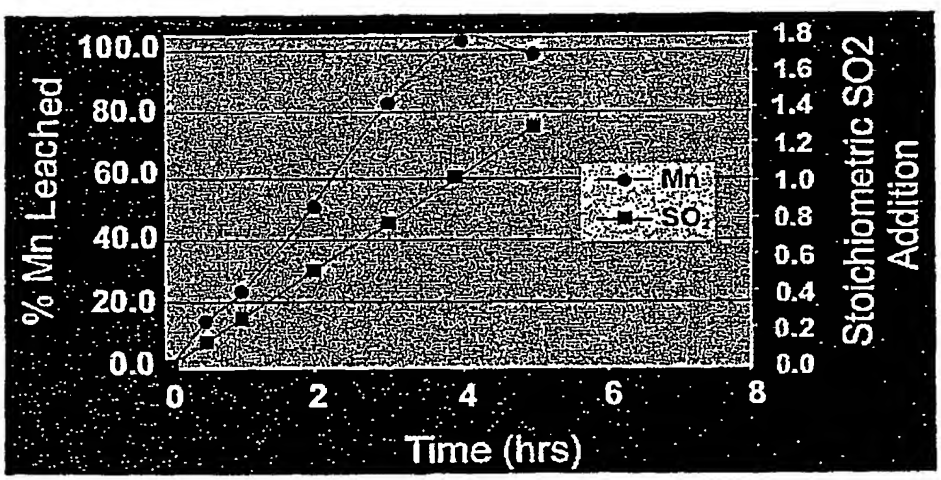

Figure 3

Sulfur Dioxide Leach